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Morphing in nature and beyond: a review of natural and synthetic shape-changing materials and mechanisms

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ABSTRACT

Shape-changing materials open an entirely new solution space for a wide range of disciplines: from architecture that responds to the environment and medical devices that unpack inside the body, to passive sensors and novel robotic actuators. While synthetic shape-changing materials are still in their infancy, studies of biological morphing materials have revealed key paradigms and features which underlie efficient natural shape-change. Here, we review some of these insights and how they have been, or may be, translated to artificial solutions. We focus on soft matter due to its prevalence in nature, compatibility with users and potential for novel design. Initially, we review examples of natural shape-changing materials—skeletal muscle, tendons and plant tissues—and compare with synthetic examples with similar methods of operation. Stimuli to motion are outlined in general principle, with examples of their use and potential in manufactured systems. Anisotropy is identified as a crucial element in directing shape-change to fulfil designed tasks, and some manufacturing routes to its achievement are highlighted. We conclude with potential directions for future work, including the simultaneous development of materials and manufacturing techniques and the hierarchical combination of effects at multiple length scales.

Introduction

Complex multifunctional materials are common within the natural world across all length scales and taxa: from the high tensile strength of spider silk [1]

and the compressive properties of bone [2], to the iridescence of the butterfly wing [3] and the fast actuation of cuttlefish skin [4]. These materials display intricate architectures across the nano-, micro- and mesoscales, allowing for an impressive array of tailored functional materials properties. Natural

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materials have long been an inspiration to the materials chemist, physicist and engineer, and using the combined toolkits of synthetic chemistry and advanced fabrication techniques, many of these materials have been successfully replicated and, in some cases, improved upon in the synthetic world (e.g. a gecko-inspired adhesive which, unlike the original lizards, also adheres underwater) [5].

However, an area where nature still outperforms our current synthetic capabilities is that of active, self-shaping and stimuli-responsive materials. Material structures found in nature must be more than just a static object, framework or skin. Natural structures need to be triggered under certain conditions, or by external stimuli, for basic biological functions to occur, and where possible exhibit multiple capabilities. What is remarkable, however, is that the variety of ways that this can be achieved across the plant and animal kingdom takes place with relatively limited chemical diversity and with large structural changes triggered under mild, ambient conditions. This forms a severe contrast to the variety of synthetic molecules and extreme environments available to human designers and suggests the existence of a wide solution space once key biological principles are extracted and understood.

Naturally, the properties of actuating materials inform the potential for further development and refinement of response, and ultimately applications. Many studies of shape memory alloys and piezoelectric materials, some of the most prominent shape-changing materials, exist—see Mohd Jani [6] and Irschik [7]—but these differ radically from the natural solutions seen around us. Therefore, in keeping with the biomimetic theme of this review, the materials focused on here will be ‘soft’ actuators—soft materials capable of changing their shape in response to stimuli. Soft materials are usefully characterised by Doi as having fundamental ‘building blocks’ on the order of 10–10,000 Å and thus having relatively slow response times between 1 and 10^4 s, a high response to stimuli that necessitates non-linear description and being easily driven out of equilibrium [8]. The subsection of soft materials that behave as actuators, capable of moving themselves or their surroundings, forms the topic of this review. As examples, this includes materials such as muscle and unfolding petals.

While soft materials depart from the traditional materials of engineering and may seem to lack

robustness, they also offer novel advantages, as detailed by Quake and Scherer [9]. They are efficient to manufacture at small scale and they can be easily integrated with hard elements as required, for instance as a valve seal. In devices, soft materials give increased compatibility with human and animal users, and greater adaptability which confers the ability to operate in unpredictable, extreme environments [10, 11]. Such behaviour has many prospective applications, from biomedical devices [12] and passive building materials [13], to microfluidics [14], product design [15] and soft robotics [10, 16].

In this article, the paradigm of self-shaping and actuating materials found in nature will be introduced, to lay the groundwork for a review of the current literature on soft synthetic analogues. Candidate materials for biomimicry of response will be identified, along with their mechanisms, limitations and triggers. It will be seen that control of structure, and therefore available manufacturing possibilities, will be crucial to realise the goal of synthetic morphing materials.

Benchmarking natural materials against synthetics

There are many examples of actuation response of natural materials to changes in environmental humidity. This can range from the simple curling of a wet leaf as it dries, to more complex processes such as self-burial of seeds [17]. The passive opening and closing of the scales of a pinecone is an elegant example of hygroscopic actuation for seed dispersal, accompanied by a simple synthetic model. The reversible movement of the pine cone scales is driven by differences in structural orientation of the cellulose microfibrils within cell walls across the structure. The microfibrils have a greater resistance to extension along their axis of alignment, and so by varying this angle relative to the body of the cell, deformation of the volume can be channelled preferentially in one direction. Cells making up the outside of the scale are orientated to elongate on exposure to humidity, whereas the inner layer are more resistant to elongation [18].

This leads to a behaviour which has been compared to that of a thermally responsive bimetallic strip, which undergoes bending due to the differing thermal responses of the two constituent metals

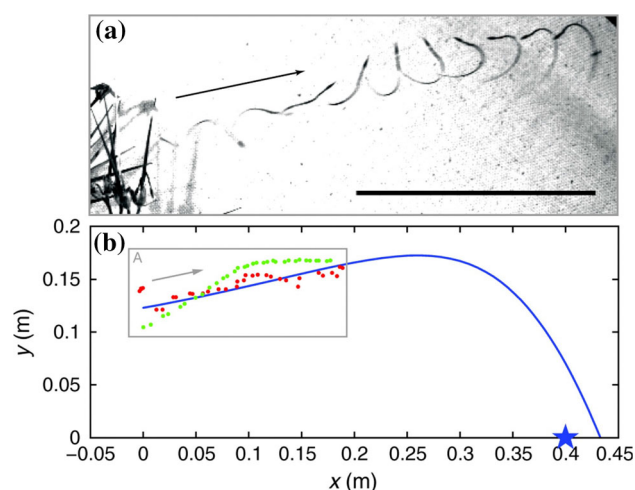


Figure 1 The capability of natural shape-change. **a** Representative launch trajectory of the filaree awn, as recorded by Evangelista et al., shown by multiple exposures at 4-ms intervals. Movement is from left to right. Scale bar 10 cm. **b** Trajectory predicted by modelling, matching the initial launch trajectory [inset box, seed (green) and tip (red) positions shown at 2-ms intervals] and final distance thrown (blue star). Reproduced from Evangelista et al. with permission from the Company of Biologists. [17] Copyright 2011.

bound together [18, 19]. This is a familiar and tractable model in engineering and physics with a long history. First modelled by Timoshenko in 1925 [20], bimetallic strips were a common control switching element before being replaced with modern relays. The form has, from the very early work on shape-changing hydrogels by Hu [21], been a simple test-case for soft shape-changing materials. Since then research in the area has blossomed, using techniques including chemical variation [21], variation in cross-linking density [22], and alignment of restrictive elements [23] to achieve controlled movement, as discussed in more detail later in this manuscript.

Cellulose catapults: a natural example

In an effort to overcome limitations in chemical diversity and operating temperature, nature programmes the sequential arrangement and orientations of individual structural units, while simultaneously tailoring their function and attachment strategies to maximise the design for survival and longevity. A key element is the transmission and amplification of small degrees of strain across the length scales. As will be described below, this can translate a relatively simple and modest response to

external stimuli into large-scale movements such as twisting, bending and opening.

Many plants exploit the principle of cellulose orientation directing moisture driven deployment, from the opening of eudicot seedpods [24] to the unfurling of the desert resurrection plant [19]. More complex behaviour is produced with more elaborate cellulose arrangements, and closer examination of this illuminates principles that may be helpful for reproducing their properties.

Erodium cicutaria, commonly known as redstem filaree (among many other names), is a small Mediterranean plant related to the geranium. Filarees disperse by firing their seeds around half a metre, powered only by the arrangement and drying of cellulose and lignin. The awn, or seed delivery mechanism, of *E. cicutaria* is a thin support which attaches the seeds to the main body of the plant, and as it desiccates curls into a spring, storing elastic energy. At a critical point, this material cracks and the elastic energy is released. This behaviour is illustrated in Fig. 1, as recorded and analysed by Evangelista et al. [17].

Within the awn, each constituent cell is encircled by cellulose in a helical arrangement. Importantly, the axis of the helix is not aligned with the axis of the cell, causing the cell itself to bend such that it packs in a helical form. Thus, the off-axis alignment of the cellulose nanostructure instigates a similar directionality in the cellular alignment, which results in the macroscopic coiling effect seen [25]. As the material dehydrates, the coil becomes tighter, storing more and more tension until the material eventually fractures. This has been successfully mathematically modelled by Aharoni et al. [26] and in a simplified version reproduced in a physical model by Abraham et al. [25]. This latter work demonstrates that one does not need to reproduce all the elegant details of the natural solution to draw on the concept.

This is all achieved with cellulose microfibrils embedded in a matrix of polysaccharides, aromatics and structural proteins—materials far removed from the inorganic chemical palette of most modern engineers. For comparison purposes, we compared the range of an equivalent volume to the filaree seed and awn (Fig. 1), composed of a variety of natural and synthetic shape-changing materials, if this were to be launched under the propulsion of its own storage energy. This provides a way to parametrise the energy stored in a fixed unit volume, while building

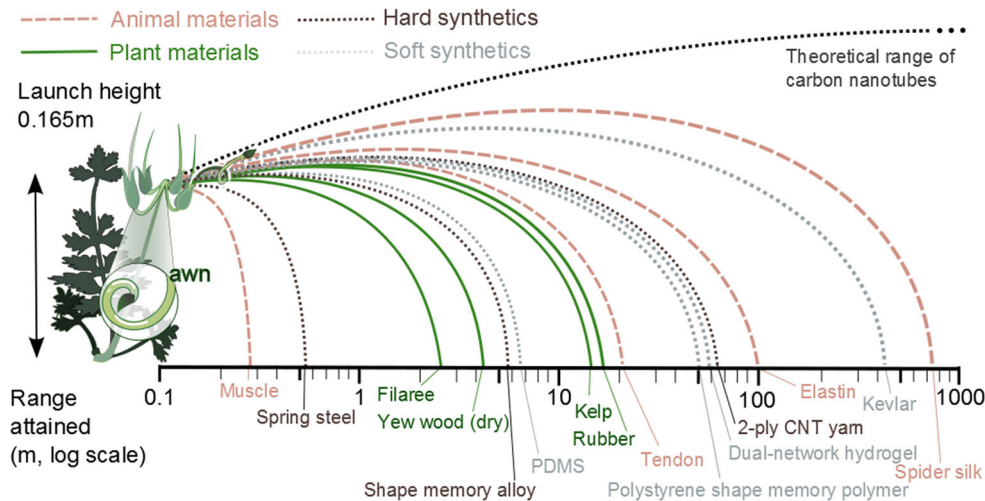


Figure 2 Comparing the capabilities of various natural and synthetic shape-changing materials, using the example of ballistic seed dispersal, which incorporates both the capacity for elastic energy storage and an allowance for density. They are compared to the natural example of the filaree, which has an energy density of approximately 750 kJ/kg and a mass of 5×10^{-3} g, enabling projection 2.62 m (without drag). Literature values and

calculations of energy density within the Hookean region are used to extrapolate range for plant (solid green), animal (dashed coral), soft and hard synthetic (dotted light and dark grey, respectively) materials. Derivation is based on the calculations of Evangelista et al., simplified to neglect drag and assume a constant volume. [17] Full details of sources and values are given in Supplementary Information.

in a penalty for greater weight. Thus, the energy density per unit weight is converted into an easy-to-visualise range of lengths, highlighting the capability of natural, low-density materials. Comparative values are shown in Fig. 2.

Our figures are derived from some simple assumptions, and the application of conservation of energy and Newtonian mechanics. We assume a cylindrical volume of which undergoes uniform contraction. Values for the stored energy contained within such a volume are drawn from a variety of sources (see supplementary information) and are drawn from both active contributions (for materials such as muscle and shape memory polymer) and passively stored elastic energy (for materials such as gels and spider silk, for which the highest strain value which remains in the Hookean region is used). These are, where necessary, converted into energy per unit mass using available measures of density (sources in supplementary information). We then assume an equivalent percentage of stored strain energy as in the filaree is converted into rectilinear motion—2 % as calculated by Evangelista et al. Finally, we take a constant launch angle and, neglecting drag, use standard calculations of projectile motion to find the range of a synthetic awn and seed.

This is not presented as a detailed analysis or a design strategy. But nevertheless it provides a simple comparison between actuating materials of different classes in terms of energy available for self-motion and highlights some features of interest. The potential of soft biological materials such as filaree and tendon is clear in this context. Their advantage derives from their low density—a crucial point for self-shaping materials that are required to move their own weight, as in many realistic applications. In synthetic competitors, both shape memory polymer and hydrogel are comparable to the best plant and animal material energy storages shown, with only dragline spider silk—a highly anomalous material which has resisted many attempts to analyse and reproduce—exceeding the capacity of our most successful synthetic by this (admittedly artificial) metric, Kevlar. Both Kevlar and spider silk are liquid crystalline in solution and achieve alignment during the process of spinning extrusion, from which their properties derive [27].

These back-of-the-envelope considerations suggest some initial areas of interest for a researcher looking into self-shaping materials through a biological lens. Gels suggest the potential of low-density, soft materials; memory polymers show a promising high-

energy density; and Kevlar and spider silk suggest the importance of molecular alignment.

It can be seen that of the animal tissues that exist inside the organism (thus exempting spider silk), pure elastin has the best performance. However, in nature, this must be used as a composite, due to the need for biological tissues to meet multiple performance requirements. This reduces their energy storage capacity somewhat. Analogously, the high theoretical performance of carbon nanotubes is unlikely to translate wholly into a practical material. However, performance can reasonably be expected to match or exceed the performance of CNT yarn, which again compares well with elastin. The ability of these efficient molecules to improve performance, even at low proportions in the material, hints at the potential of nanoinclusions and other composites.

We therefore see that to emulate the complex actuation observed in the stork's bill awn and other natural morphing systems, we require knowledge of the inherent properties of the material (the swelling matrix), the stimuli (the conditions or trigger required, for example the magnitude of dehydration the plant will experience), the reinforcement architecture (the direction of the fibrils and their hierarchical assembly), and the cost in energy for actuation. Without waiting for 4.5 billion years for evolution to produce protein machines to conduct this assembly, we should also consider methods of manufacturing these structural features.

These topics will inform the rest of the review, which will address some prototypical natural morphing materials and related synthetics, run through triggering stimuli including hygroscopic, chemical, heat, light and electrical and magnetic inputs, and finally discuss methods of modifying such materials in order to direct the response in a programmed direction. We conclude with some promising future directions.

Natural morphing materials and synthetic substitutes

A vast amount of actuating soft materials exist, including shape memory polymers (SMPs), hydrogels, elastomers and liquid crystals. This library only expands when the potential for composites or alternative processing is considered. The addition of secondary materials may enhance properties such as

tensile strength, compressive strength, toughness and elasticity, or confer response to external stimuli. Therefore, this section aims instead to focus on a few key natural actuating materials, discuss the principles at both the micro- and macroscale by which each operates, sketch an option for artificial emulation and its mechanism, and provide an overview of their potential uses and limitations. We will highlight bio-inspired and otherwise notable uses of the material, alone or as a composite, and where relevant applications.

Numerous reviews are available for a deeper look at the topics united in this review. Broad sketches of actuating polymers and polymer gels are provided by Behl, Ahn and Geryak [28–30], and composites by Meng; [31] more specific reviews will be highlighted as topics are discussed. We are indebted to Ionov for his informative division of polymeric actuators according to their working principles [32], from which we draw inspiration for our comparison of natural actuators with similar artificial systems.

Skeletal muscle—active contraction

The most obvious example of a natural actuator is muscle, a tissue specialised to decrease in length when free to move or increase in tension when constrained. This is achieved using hierarchical principles, triggered by the presence of calcium ions, and produces macroscale contraction from staggered fibrous structures.

Within each muscle cell are filaments known as myofibrils, formed from small cylindrical units, sarcomeres, interspersed with Z-discs (Fig. 3). Hundreds of thin filaments of the protein actin are attached to the capping Z-discs at each end of the sarcomere, and thick filaments of myosin float freely, interdigitated with the actin filaments at both ends. The release of Ca^{2+} ions causes the myosin heads at both ends of the thick filament to pull on the anchored actin filaments, reducing the distance between Z-units and thus the length of the sarcomeres by around 70 % [33].

This effect is magnified to the microscopic level by multiple, aligned myofibrils, formed from sarcomeres packaged within stabilizing proteins, notably the stretchy, massive protein titin, which gives the muscle elastic properties and keeps the arrangement in place [34]. Thousands of these sub-units make up a single myofibril, which are aligned inside the muscle

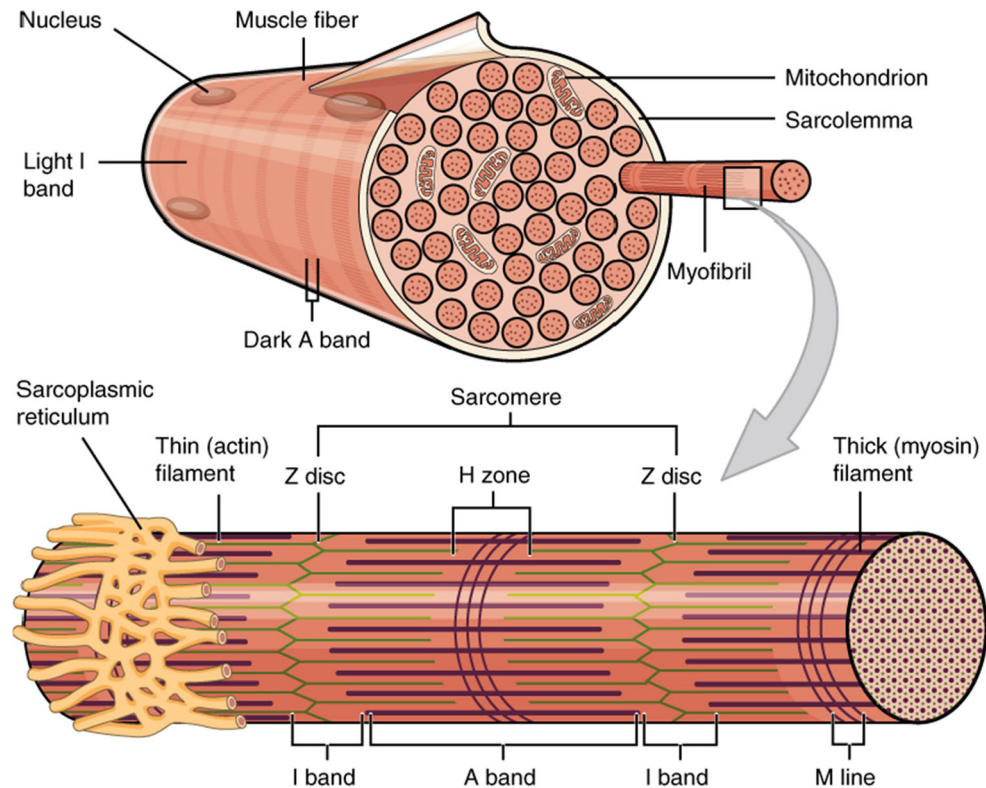


Figure 3 The hierarchical structure of muscle, an active contracting material. A skeletal muscle fibre is surrounded by a plasma membrane called the sarcolemma. Inside, the muscle fibre is composed of many fibrils, where each fibril is composed of sarcomeres, the individual units of contraction. A ‘Z-disc’ at either end is attached to thin actin filaments (shown here in *green*), with

thick myosin filaments in between (shown as *thick purple lines*). Motion is achieved by the grasping of actin by myosin, which draws the filaments together. Reproduced from Anatomy and Physiology under Creative Commons Attribution License 4.0 from OpenStax. Copyright 2016.

cells. Muscle cells are then bunched into fascicles, which define the direction of contraction of the muscle tissue, and inform the complex motions enabled by muscles. These range from the 486 ms^{-2} acceleration achieved by the chameleon’s tongue [35] to the exquisite shape control of cuttlefish papillae [4]. The degree of macroscale muscle contraction varies between approximately 20–40 % [36].

Artificial systems in which molecular-scale structures change position or orientation upon the application of an energy source, causing a change in dimensions while retaining approximately constant volume, include liquid crystals [37] and ionic-polymer metal composites, [38] among other electroactive polymers (EAPs) [39]. This latter is a very large category containing multiple methods of actuations, from the piezoelectric behaviour of some organic polymers to the high-performance behaviour of carbon nanotube supercapacitors. Due to limitations of space and their potential for anisotropic structuring,

we focus on liquid crystal elastomers (LCEs) as a synthetic analogue for muscle. However, the reader is directed to further reviews for more information on EAPs and related systems [40–42].

Shape-change of these materials is an active process, necessitating constant stimulation, and thus power use, to retain deformation. This permits control, both remote and local, but limits efficiency and independence of operation. However, this is also a feature of well-established synthetic actuation methods such as hydraulic or piezoelectric control and so should not be necessarily be regarded as a disqualification.

Comparisons between liquid crystals and biological muscles have a long history, beginning with the original proposal and theoretical analysis by De Gennes in 1975 and continuing to the present day [43–46]. This well-understood state of matter exhibits a shift in stiffness [47], volume and optical properties as a result of changes in the internal order of rod-like

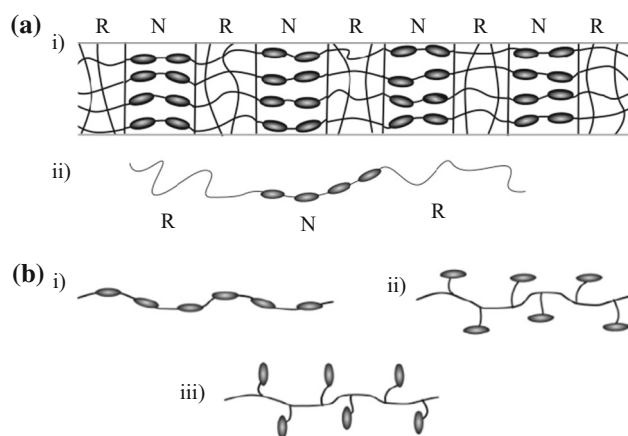


Figure 4 Sketches of the structure of LCEs and their analogies to muscles. **a** A striated artificial muscle after de Gennes (1997) (i) based on a triblock copolymer RNR (ii). Shown here in a lamellar phase with the elastomer part R cross-linked. Similarities to the structure of muscle fibrils (shown in Fig. 3) are clear, with the domain R replacing the Z-disc and the aligned mesogenic units performing similarly to the interpenetrating fibrils, although changing shape via extension rather than contraction. **b** Options for attachment of mesogenic liquid crystalline (LC) groups (denoted by shaded ovals) to elastomeric polymer backbone: (i) main-chain LC polymer; (ii) side-on side-chain LC polymer; and (iii) end-on side-chain LC polymer. Any of the configurations illustrated in **b** may be used in block N of **a**, demonstrating the diversity of LCE chemistry possible. Adapted from Li et al., with permission from John Wiley and Sons [205]. Copyright 2004.

sub-unit mesogens. LCs are found throughout nature, from spider silk to retinal proteins [27], although as yet the reason for the prominence of this state is not clear. However, studies of insect wing muscles have yielded crystalline forms under X-ray [48], demonstrating that at least some kinds of muscle structures benefit from high levels of order. It is also known that cell membranes are composed of liquid crystalline structures with various phases. Their function is the subject of ongoing research, but it is thought they may play a role in cell division and response to external influences [49]. As synthetic actuators, liquid crystals are bound to polymers, which are cross-linked to form a structural role analogous to titin in muscle; [34] the backbone provides a flexible anchor for the mesogenic groups as they reorientate, allowing the recovery of some strain. As the sub-units are aligned the polymer network is stretched: as the external stimulus is removed, it recovers a more entropically favourable coiled configuration. The combined system is known as a LCE and was initially developed by Küpfer and

Finkelmann [50]. Figure 4a shows a schematic of a liquid crystal elastomer reminiscent of a muscle (i), and the polymer sub-unit which would make it up (ii).

Mesogenic units may be connected via an element on the short side ('end-on'), in the middle of the longer side ('side-on'), or within the backbone itself (shown in Fig. 4b) and may be joined to an existing backbone, polymerised, or cross-linked and polymerised in one step [51]. Commonly used mesogenic units include azo-containing groups, which under photostimulus shift from a rod-like trans isomer to a kinked cis-version. This change in shape results in a photo-induced change in packing, and therefore volume. This was demonstrated by Tsutsumi and compared to theory by Hogan et al. [52, 53]. Mesogens with acrylate or methacrylate moieties, which are readily polymerised, may be varied to adapt the material properties. ABA triblock copolymers allow the construction of alternative structures, such as dilute gels [54]. Options for components and synthetic routes are discussed by Ohm [51], and other useful reviews may be found in Jiang et al. [55], Chambers et al. [56], and White et al. [37]. Existing issues and open questions are highlighted by Urayama [57].

The direction of contraction depends on the axis of alignment for the mesogenic units, known as the director, and analogous to the myofibril direction. This may be constant throughout a material, creating simple uniaxial deformation of up to 300 %, or vary in orientation creating twists [58] and out of plane effects [59]. Programmable orientation of the director in discrete volume elements across an LCE was demonstrated in 2015, unlocking arbitrary deformation through 'voxelation' [60]. This enables the exertion of greater forces, as the 55 % contraction attainable in a single element of the material is amplified by local forces to give a 3000 % stroke. Additional larger scale structure may be imparted by soft lithography, such as the work by Buguin et al. in using soft lithography to create forest of thermo-responsive LCE micropillars, suggested as tiny artificial pumps or switchable surfaces [61].

Tendons—release of stored energy

A second large-scale division of actuation materials is those that are capable of storing energy and, when triggered, causing deformation. This may result from

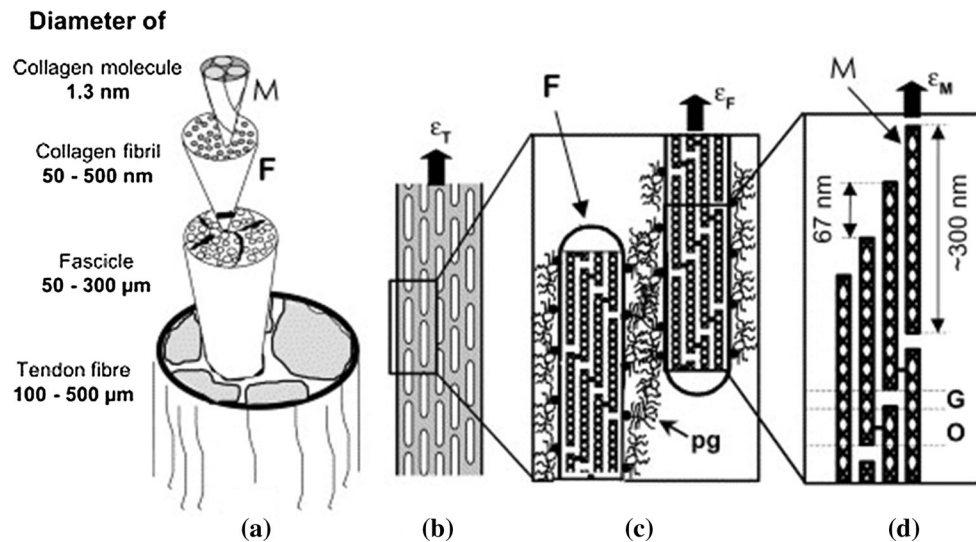


Figure 5 The hierarchical structure of tendon, an energy storing material. **a** Simplified tendon structure. Tendon is made of a number of parallel fascicles containing collagen fibrils (marked F), which are themselves assemblies of parallel molecules (marked M). **b** The tendon fascicle can be viewed as a composite of collagen fibrils (having a thickness of several hundred nanometres and a length in the order of 10 μm) in a proteoglycan-rich matrix,

subjected to a strain ε_T . **c** Some of the strain will be taken up by a deformation of the proteoglycans (pg) matrix. The remaining strain, ε_F , is transmitted to the fibrils (F). **d** Triple-helical collagen molecules (M) are packed within fibrils in a staggered way. Reprinted from Fratzl, with permission from Elsevier. [64] Copyright 2003.

the simple removal of the initial stimulus (in the case of elastomers), or require an additional trigger to escape a local energy minimum and release the internal stored energy. The first case is analogous to many elastic tissues in animals, for which tendons will be our example. The second is rarely seen in nature, but forms a large class of interesting engineering materials known as SMPs.

Tendons are viscoelastic tissues composed of collagen, which connect muscle to bone and in some cases, depending on their anatomical role, may also exhibit energy-conserving elastic properties [62]. Like muscles, they too show hierarchical structures with liquid crystalline order (Fig. 5). The smallest element of collagen, the tropocollagen molecule, consists of three intertwined helices which are then cross-linked into fibres, wound into fibrils, and grouped into fascicles to form a tendons [63]. It is notable that the strain of the fibre is exceeded by that of the fibril and subsequently of the fascicle: in other words, the hierarchical structure ensures the properties of the whole are greater than the sum of the parts [64].

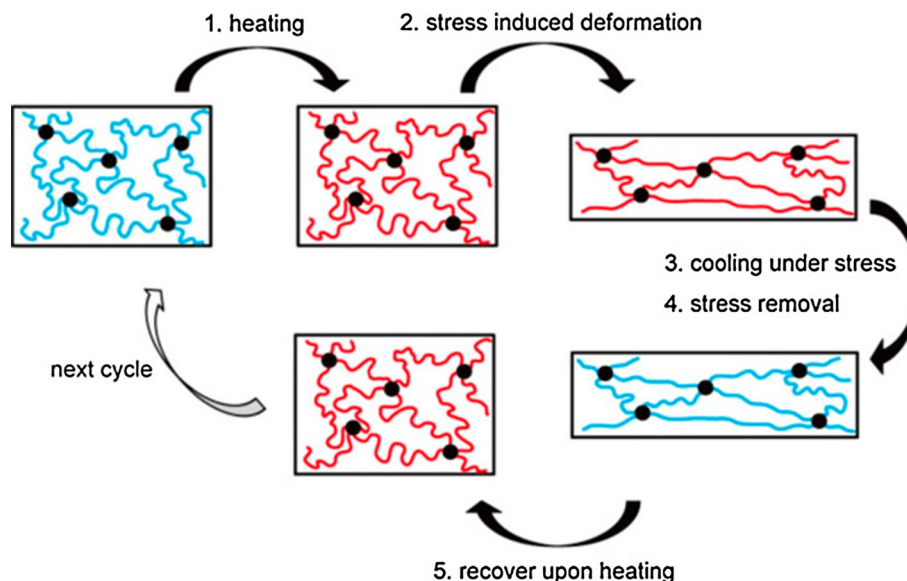
Healthy tendons have been suggested to be auxetic, showing an absence of Poisson's contraction when subjected to uniaxial stress. This unusual property is thought to derive from the varying angle

of collagen fibrils throughout the fascicle, which was observed to vary depending on the biological role of the tendon, and affects its elastic response [65]. This is notably efficient: under stresses of 20 MPa and frequencies of 1–2 Hz, tendon tissues were shown to return up to 93 % of strain energy [66].

Shape memory polymers are somewhat analogous in that they derive their ability to reshape from an external applied deformation, which is translated into stored energy in the material and upon release enables a return to the original shape (see Fig. 6). However, in the case of SMPs, they may be 'set' into an intermediary shape and remain there indefinitely, until the input of sufficient additional energy.

At a microscale, the behaviour arises from a system of netpoints, which may be physical or chemical bonds, and connecting chains which switch their flexibility under different conditions, the most common of which is a change in heat [67]. In a typical application, the system is heated above the glass temperature of the chain sections, when they become flexible. It is then deformed by an external force while cooling occurs to below T_g , 'locking' the chains in place in a high-energy state. When the temperature is raised above T_g , the chains regain mobility and release strain to gain entropy, and return to their

Figure 6 The molecular mechanism of a dual shape memory polymer throughout a thermal cycle. *Black dots* netpoints; *blue lines* molecular chains of low mobility below transition temperature; *red lines* molecular chains of high mobility above transition temperature. Reproduced from Zhao et al. with permission from Elsevier. [70] Copyright 2015.



original maximum entropy state, corresponding to the relaxed macroscopic shape.

Recent experimental work on feathers and hair have identified shape memory behaviour in keratin-based natural materials [68, 69]. As seen in human hair styling, deformation can be set in by, for instance, wrapping around a curler while wet, but the original form will be recovered when wetted again. The authors hypothesise that in these materials, a combination of crystalline regions, chemical bonds, and hydrogen bonds act as netpoints to hold the molecular shape. Hydrogen bonds are removed from their original position when water penetrates the hair, leaving just chemical and crystalline netpoints to hold the polymers in place. These may be distorted away from their lowest energy configuration during drying and form temporary hydrogen bonds to lock in the temporary shape, but upon the addition of more water, the netpoints relax again into the original shape. Xiao and Hu suggest that different ratios between chemical and crystalline netpoints derive from the protein makeup of the hair and cause different fixity ratios of hairs from different individuals [68]. However, there is still much work to be done before the body of research on natural SMPs is as rich as that existing on tendon.

Synthetic SMPs have been demonstrated that show multiple shapes, cycling between three or more intermediary stages with varying stimulus intensity (multi-way SMP), and that can reversibly cross between two programmed states, rather than just returning to the lowest energy state (2 W-SME) [70].

In addition to heat, SMPs have been developed which respond to light [71], magnetism [72] and hydration with cooling [73]. A major advantage of SMPs over other shape-changing materials mentioned so far is their programmability, which enables them to take multiple forms and functions. Existing limitations for SMPs have been given as a low-energy storage modulus, limiting their force and stroke, a slower response time than hard materials, and a deterioration in response to repeated cycling [74].

The family of SMPs is large; as a start, any copolymer combination with different glass temperatures for each section fulfils this requirement, with the polymer of highest T_g acting as the netpoint. Beyond the possibilities of chemical diversity, the thermal, structural and shape memory properties for a given combination may be modified by adjusting the molecular weight of each polymer component [75], the molecular architecture and temperature history [76]. Post-synthesis manufacturing techniques also affect response, as shown by Zhuo et al. when varying the voltage and solution concentration of electrospun polyurethane nanofibers [77].

Further possibilities are opened by the addition of composite reinforcement materials, such as nanocellulose [78] or CNTs [79, 80] although it should be noted that composite reinforcement is far from a magic bullet and may in fact degrade SMP performance [81]. The reader is referred to a number of excellent general reviews of SMPs and their composites [82–85] for more exhaustive assessments of previously studied polymers and their properties. A

focus on electrically active SMPs may be found in Liu et al. [86].

Plant tissues—volume-change

As seen in the earlier example, plants achieve large, complex actuation as a result of relatively modest changes in volume. Examples abound, from the opening of leaves and tracking of the sun, to the projectile dispersion of seeds and spores and the clasping of climbing tendrils.

Swelling-based actuation occurs over a timescale of milliseconds to hours and crosses length scales from stomata on the leaf surface, composed of just two cells, to the entire plant structure [87]. The pulvinus, an organ found at the base of leaves and inside the stem, consists of internal cells that swell and contract [88]. This enables plants to track the sun with leaves or flowers, and modulate their temperatures and rates of photosynthesis. A wide number of angiosperms have been studied, including alpine flowers [89] and the Cornish mallow [90].

Volume-changes may be combined with other structural features to achieve faster responses through the sudden release of energy stored in other formats. Fracture-based launching was discussed in the context of the filaree awn and may also be seen in flowers [91]. The Sporangium fern exploits cavitation effects caused by a drop in pressure as volume is redistributed to catapult its spores onwards [92, 93]. The Venus flytrap exhibits a bistable structure which, when stored elastic energy from turgor pressure crosses a threshold, triggers rapid curvature in a perpendicular direction on the plane [94]. This enhances the response rate of a turgor-based system sufficiently to capture highly mobile prey.

Approaches to plant-based actuation and emulation are thoroughly covered by Fratzl and Burgert [95]. A common starting point has been selective reinforcement of materials that swell in response to hydration, often hydrogels—three-dimensional polymer networks, as little as 0.5 % w/w, swollen in solvent. Interestingly, responsive hydrogels made of pectin are found in the vasculature tissue of plants, which react to increasing ion concentration with corresponding changes in volume that modify the uptake of liquids [96]. Hydrogels as a class are typically brittle, slow to reach maximum deformation, and exert a limited force. However, their ease of processing and modification, as well as their

demonstrated efficacy in natural systems, makes them a well-used model system with potential uses in biomedical fields [12, 97, 98].

Hydrogels may change volume by as much as 1100 times [99] in response to chemical, hygroscopic, heat, or light triggers, and may also exhibit shape memory characteristics [70, 100]. Properties depend on cross-link density, choice of polymer, copolymer or blend, nature of cross-link bonding [101], and solvent. In addition, structured or unstructured reinforcement may be added. Well-studied hydrogel chemistries include synthetics such as acrylamide, PEG and PVA, and biopolymers such as cellulose [102] and gelatin [103]. A general review of the theory used to understand stimuli-responsive hydrogels, and the multitude of work on the subject, can be found in Koetting [104].

While they are easy to work with and share similarities with some biological materials, hydrogels hold two major drawbacks; their slow response time and their lack of mechanical strength. Their need for hydration is also a challenge. However, the recent success of dye-sensitised solar cells, which are achieving commercial success despite currently relying on a corrosive liquid electrolyte, suggests this does not necessarily disqualify a technology [105]. As Calvert has commented, fruits such as oranges require hydration and yet may be transported across the world without issue [106].

Swelling response is diffusion-based and shows a power law relationship between time and length scale [107]. Response rate can be increased with the addition of microchannels [108], mimicking the operation of vasculature and allowing integration into microfluidic devices. Addition of graft chains, creating a comb-type hydrogel, has also been demonstrated to improve the response speed of some nanocomposites by around a factor of three [109].

Hope for strong hydrogel-based devices is inspired by the properties of gels seen in nature. Synthetic hydrogels typically have fracture energies of about 10 Jm^{-2} ; cartilage, meanwhile, withstands an additional two orders of magnitude, fracturing at around 1000 Jm^{-2} [106]. Many strategies are currently being employed to strengthen hydrogels, including double networks, composite addition and structural modification, but there is a long way to go before their potential can be fully realised [110].

Possible solutions are improvements in gel nanostructure or microstructure. For example, the 20 % of

20 nm collagen fibres found in the cornea are theorised to be the source of its 4 MPa tensile strength [106]. A similar concept was demonstrated with fibre reinforcement of an epoxy-based hydrogel, increasing its breaking stress by a factor of 20 [111]—despite to retain other properties simultaneously, the fibres would need to be significantly smaller, as seen in the cornea.

Modification of nanostructure has been able to produce hydrogels with a large swelling ratio, rapid response rate and elastic properties that permit extensive deformation without fracture [112]. In a two-step synthesis, functionalised nanogels of less than 100 nm in diameter are created, which are then subsequently joined together. This approach generates heterogeneous mesh-like structures relatively easy, suggesting biomimetic hierarchical nanostructures need not require extensive manufacturing.

Beyond the modification of structure, the addition of nanocomposites to hydrogels may confer still more properties [113]. Nanoparticles (NP) such as silicates and metal oxides can promote cross-linking, increase strength and modulate shear response. In particular, metal oxide NPs can add an orthogonal degree of responsiveness [114], improve conductivity [115] and give additional properties such as antimicrobial activity [115]. Cellulosic polymers have been used to sensitize hydrogels to temperature, pH and redox potential [116]. More information on hydrogels can be found in Ionov [110, 117].

Remote control: stimuli to shape-change

A major influence on the potential applications and development of responsive materials is, of course, how they can be triggered into movement. Again, natural systems operate with a limited palette of stimuli, with the vast majority of actuation being achieved by hygroscopic and chemical gradients. These are familiar to us in everyday life: the wilting and blooming of flowers and leaves arises from hydroscopic triggers, while muscle contraction is mediated by Ca^{++} concentration within the myocytes.

In the artificial world, the prospects for remote control and integration with existing systems make light and electrical and magnetic fields attractive candidates for controlling response, and raise the possibility of moving beyond natural capabilities.

Hygroscopic

Hydrogels are the prototypical material for hygroscopic response, changing in size over 1100-fold when solvent particles have fully infiltrated their polymer networks and caused expansion through hydrophilic effects [99]. However, other polymers and LCEs [118] can also show this property as the networks hydrate. Overall global swelling of polymer networks may be controlled by the use of different solvents [119], while local swelling may be modulated via modulation of vasculature [120], chemical composition [121] or altering of cross-link density [122], for example via ionoprinting [123]. In the case of LCEs, deformation is anisotropic and determined by the direction of mesogenic alignment [118]. Variation in swelling across a hydrogel sample may be used to move the hydrogel itself [124], surroundings [125] or inclusions [126].

In shape memory networks with polyurethane, the shape memory effect may be triggered by percolation of water or other low molecular weight solvents through the network. The presence of the water lowers the glass temperature of the cross-linking polymer to below ambient, whereupon the material returns to its original conformation [127, 128]. The example system of pyridine with polyurethanes attains shape recovery of over 90 % following this stimulation [129].

Cellulose has been used as a reversible support to confer responsive reinforcement to polymers, in an example of tunicate biomimicry. Surface hydroxyl groups on cellulose nanofibers have strong tendency to associate with others, which is reversible with hydration. Capadona et al. demonstrated a switchable 40-fold change in the tensile modulus of their system and suggested applications in electrodes and medical devices [130]. Reversible hydrogen bonding between cellulose fibres provides another way to modulate the shape memory effect in polyurethanes, independent of thermal contributions [131].

The ability of the pine cone, wheat awn and other plants to undergo humidity-responsive actuation has provided inspiration for a simple biomimetic model system, consisting of paper (the active, cellulose containing component) glued onto a flexible polymer [18]. This mimic undergoes more complex actuation behaviour than the natural systems but is sufficiently robust to create a “flower” which can open and close in response to wetting over timescales of around an

hour. Many related systems have been developed, for applications ranging from walls which open to provide venting in warm weather [13] to a synthetic leaf that wilts when tea is brewed [15], and a hygrosopic generator [132].

Chemical

Presence of chemical species is a ubiquitous natural trigger, whether this be ion concentration, pH change, or presence of a specific antigen. Volume-changes resulting from chemical triggers to hydrogels may reach 350-fold [133]. Polymeric thin films such as SU-8, a commonly used photoresist, may also be treated to show bending responses to solvent stimuli [134].

To create a polymer hydrogel that is sensitive to pH, acidic or basic functional groups must be added to the polymer backbone or side chains. As the pH of the aqueous medium contained within the hydrogel is altered, the polymer will release or accept protons which will trigger a response within the gel. For example, as the pH of an acidic gel is raised, the degree of ionisation of the polymer increases, which leads to electrostatic repulsion and swelling of the gel. A reduction in pH would lead to swelling in a basic polymer-based hydrogel. This swelling response of pH-sensitive hydrogels has been rigorously analysed by Brannon-Peppas in terms of Flory–Huggins and rubber elasticity theory, with added contributions from ionic interaction [135]. pH-responsive hydrogels are considered strong candidates for drug delivery due to their potential in sensing and targeting [12].

DNA reactive materials could be an interesting addition to the current growth in synthetic DNA construction and design. Hydrogels have been developed that selectively contract when exposed to specific antigens [136] and single strands of DNA [137], the latter with measurable difference in response to only one base change. These are suggested for use as DNA-sensing devices or DNA-triggered actuators. Double network shape memory hydrogels have been created with two artificial DNA sequences, one pH-sensitive and one double-stranded, conjoined to acrylamide. These gels turn quasi-liquid when exposed to selected pH levels which remove one network, but can recover their pre-programmed shapes using the secondary duplex DNA network [138, 139]. Microscale DNA-responsive

hydrogel devices have been developed that are capable of bending in response to their chemical environment, and even selectively detecting, trapping and releasing bacterial cells [140].

Solvent-responsive polymers may be combined with flexible electrodes such as graphene to create self-rolling actuators and sensors for uses such as operation in confined spaces, as wearables and tools [141].

Applications shown for chemically responsive hydrogels include liquid microlenses composed of a ring of hydrogel enclosing water. This swells in response to pH, raising the meniscus within it, and has been formed into an insect-inspired compound eye, suggested for diagnostic or lab-on-chip application [142]. Eddington et al. demonstrated an internally self-regulating valve which maintained a constant pH due to the swelling and contracting of a pH-sensitive hydrogel blocking the inlet [120].

Dicker et al. propose a synthetic analogue to the sun-avoiding Cornish Mallow leaf, using a chemically responsive hydrogel rendered light-sensitive with the addition of photobase, with particular applications for passive control of solar panels [143]. Finally, cyclic motions are also possible: a Belousov–Zhabotinsky oscillating chemical reaction has been demonstrated in a hydrogel, creating a cyclic ‘walking’ motion reminiscent of self-sustaining responses seen in biology [144].

Heat

Thermal response is perhaps the best-known trigger for passive motion in the artificial world. Varying thermal coefficients are easy to observe, and bimetallic strip-based control systems have adopted this approach since the eighteenth century. Many commercial plastics such as polyesters and polyurethane are thermoplastics exhibiting the shape memory effect, due to their ease of processing. However, their use in post-manufacture shape-changing applications is currently novel.

A feature of soft matter is that its characteristic energy levels are on the order of the thermal fluctuations in the environment, and therefore, many examples of thermo-responsive self-shaping soft matter exist. The solvent-polymer interactions which mediate the hydrogel volume-change are temperature dependent, as is the mobility of SMP netpoints.

LCE orientation changes and cis/trans switches also occur around room temperature thermal energy.

The balance between the entropic and enthalpic energy of polymers in hydrogels is necessarily temperature dependent, and for some hydrogels, there exists a point such that their polymers switch from a hydrophilic to a hydrophobic state. To minimise energy, they undergo a coil-globule transition, shielding hydrophobic sites and gaining in entropy from collapsing into a less stretched configuration. This decreases the space between them, ejecting solvent and losing volume. The temperature at which this occurs may be adjusted by the temperature of processing [145], blending [146] and microstructure [147], in addition to the inclusion of composites which may adjust temperature response through density changes [148], or Joule or surface plasmon resonance heating (see later sections on light, electricity and magnetism for these mechanisms).

The bending of a hydrogel bilayer rod with one thermo-responsive face was demonstrated by Hu and co-workers in 1995 [21] and modelled as a bimetallic strip. More modern work has explored different approaches to the creation of gradients or conjoined materials with different properties, as detailed in the final section.

There are many suggested applications for thermo-responsive materials, including power generation through body heat, self-opening curtains [149] and thermal control valves [150]. Kim et al. demonstrated a responsive hydrogel surface which could expose or reveal arbitrarily shaped functionalised regions in response to temperature, suggested for use in lab-on-chip diagnoses [151].

Light

Use of electromagnetic or radiation sensitive material opens up opportunities for remote activation and graduated stimulation compatible with existing control systems. Liquid crystal-based systems are well-known for their light response, triggering the trans-isomer switch referred to earlier. For LCEs, polymer systems and hydrogels, the addition of nanoparticle composites with tuned plasmon resonances have been shown to add photo-response by triggering heating [109, 152, 153].

The degree of response can be modulated by varying composite proportions. Zhang et al. [154] noted that the percentage of carbon nanotubes in a

thermosensitive hydrogel material affects hydrogel response time to both optical (near IR) and thermal stimuli. They use these materials as heat-activated hinges attached to solid plates, and by varying the weight percentage of additives are able to adjust the response speed of petals opening on a model flower as a function of distance. Similar effects have been achieved by others using gold NP [155] and magnetite particles [109].

Materials with two modes of response to optical stimuli open up interesting possibilities for feedback loops. Camacho-Lopez et al. demonstrated a dye-doped LCE capable of spontaneously ‘swimming’ in a variety of surfactants: as the material is struck by light and expands, it dips below the surface, and in darkness shrinks and rises once more to complete the cycle [156]. The swimming action is directed away from the light source, which therefore is a potential source of directional control over a self-maintaining feedback loop, similar to those seen in many natural systems.

A similar bi-directional response from UV-responsive thin polydomain liquid crystal network films can be controlled by varying the polarisation direction of the light source. Oscillating the source polarisation direction therefore gives a method of optically controlling a cantilever [157]. A hydrogel micro-cantilever has also been shown to respond to UV illumination via expansion of the illuminated side and therefore bending, but this is so far irreversible, suggesting applications for light-triggered final assembly of microdevices rather than control [158]. The use of LCE sensitive to different wavelengths of light within the same system demonstrated the potential for complex behaviour achieved in situ with optical triggers [159].

It is also possible to use light to control optical systems, which suggests passive sensor applications. For example, soft liquid hydrogel microlenses can be remotely focused with IR light, and this is suggested for applications in endoscopy [160]—in contrast to the earlier-mentioned use of chemically responsive hydrogels which require direct stimuli but combine the functions of sensing and actuation. Koerner provides more information on light-triggered polymeric systems [161].

Electrical and magnetic

The electrical pulse of the action potential is a key stimulus to actuation and shaping in the natural

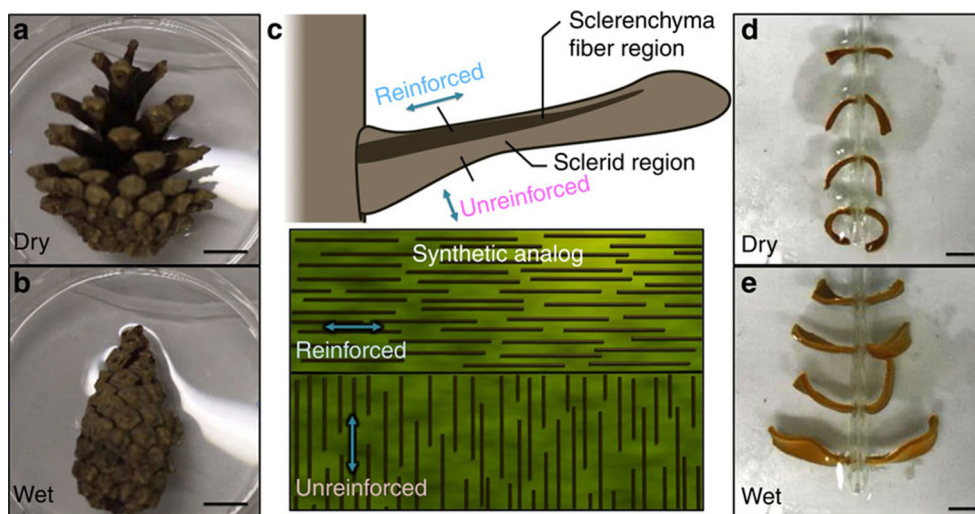


Figure 7 Pinecone biomimicry by Studart and Erb, using ultra-high magnetic response plates. **a, b** The natural principles of expansion and contraction in response to humidity. **c** (Above) diagrammatically the positioning of fibrous stiff cells (sclerenchyma) and short amorphous cells (sclereids) which give rise to the anisotropic movement of the pinecone, and (below) a schematic showing the synthetic reproduction of these properties

world, where muscle contraction results from ion channels opened by voltages on the order of 10 mV [162]. Synthetically, multiple electroactive shape-changing polymers are known, of which none exhibits the high gain of the muscle interaction: indeed, many require kilovolts to match the modest 20 % contraction of muscle [163].

A broad range of electroactive polymers are described in Bar-Cohen's canonical book on the subject [39] and have now been an active area of research for 30 years—however, no clear leader appears to be emerging in the field and we would refer an interested reader to the aforementioned book, reviews by Mirfakhai [163], Otero [164] and Baughman [165] for a deeper look at the subject. Early studies by Baughman showed the potential of carbon nanotube actuators [166], which have the advantages of low mass density, high mechanical strength and two directions of response depending on current direction. More recently, novel forms of carbon have been combined with conductive polymers, to improve the performance of said polymers while retaining their low cost and ease of processability [167, 168]. Flexible carbon-based materials may also be used as electrodes and in electrolytes, enabling the creation of multipurpose actuators that are also supercapacitors [169].

with magnetic orientation of reinforcement. **d, e** The results; responsive synthetic pinecone scales produced with selective orientation within a gelatin matrix, in a similar bilayer structure, in both dry and wet states. Reproduced from Studart and Erb with permission from the Royal Society of Chemistry. [23] Copyright 2014.

The addition of conductive elements to trigger heating, and therefore thermoresponse, can be applied to hydrogels, LCEs and SMPs. This essentially reduces down into the earlier section on thermal triggers, with additional potential for control and integration [86, 170]. Felton et al. demonstrated this approaching using Joule heating to trigger a sequence of plates connected by SMP hinges to fold into both an origami crane [171] and a walking robot [172].

Magnetic NP, commonly ferrites, may be added to hydrogels or SMPs to confer magnetoresponse upon these materials. This may act directly via the orientation of the magnetic domains in an external field, or through induced heating effects that then trigger a thermoresponse [173]. This methodology permits control of the shape memory effect by varying magnetic field strength and offers potential for 'topping up' the internal heat via induction effects, thus reducing the external temperature required to trigger [72]. Magnetic NPs may be blended into LCEs [173], SMPs [174] or hydrogels [170], or cross-linked into the polymer backbone [175].

The inclusion of magnetic NP enables magnetic fields to be used to guide microdevices including surgical microgrippers [176] and pollution-sensing fish [177].

Beyond isotropy: modification of structure

In order to achieve meaningful and complex material response, it is necessary to control the degree of sensitivity to stimuli, and also its direction. Non-trivial responses require some form of anisotropy in either the stimuli or the material. The former approach is easy in the case of electromagnetic fields or radiation, but less so for diffuse hygroscopic or chemical stimuli. Since these are the two most commonly found triggers in biological situations, evolved solutions tend to focus on manipulating the response through material structure, as seen in the earlier example of the wheat awn constrained in its swelling by fibre directionality. This also has the advantage of being independent and self-contained, although it carries the disadvantage of not being reconfigurable—often referred to as ‘programmable’ in the literature. Shape memory materials offer the prospect of resetting target and intermediate shapes, but require intervention to achieve this—holding a material curled, or stretching it, while it cools.

There are multiple ways to analyse and learn from natural material features, which have merit in different situations. For the purposes of this discussion, we have found it helpful to consider the distinction between how material properties are achieved, and the role they play for the organism overall. Using the filaree awn as an example, the variation in contraction direction is caused by fibre alignment. However, this varying contraction is used to create a spiralling structure which winds itself more tightly as it dries before breaking. So, a researcher looking to learn from the awn may choose to emulate orientation and alignment of constrictive elements, or the behaviour of a tightening spiral approaching breakpoint.

As seen with mimicry of the filaree awn [25], shape-change may be reproduced without using the same method seen in the natural example. Conversely, we will draw attention to some ways of reproducing the aligned or graded structures that give rise to shape-changing properties in nature which have not yet been used to create synthetic shape-change. Together, we hope that this palette of options will spark ideas for how biological features may be emulated, and encourage researchers to keep an open mind regarding routes to the desired outcome.

Reproducing positioning and orientation

One-dimensional elements such as fibres and rods may restrict the movement of their surrounding matrix in a given direction, as noted above for plant cells. Alternatively, aligned one-dimensional elements may create one-dimension contraction, as the myofibrils do in muscle tissue [178], or expansion. We see that placement and orientational control at nano- and micro-length scales would be necessary to emulate these features.

Mesogenic elements in liquid crystals determine the direction of actuation [179]. Various methods of alignment are used to obtain single-crystal monodomains, which ensure these elements act together. Shearing surface force [44], electrical [180] and magnetic fields [61] are all well-known methods for aligning mesogens before initiating polymerisation to preserve this orientation. Photoalignment can create spatially varying responses in two dimensions, demonstrated both continuously [181, 182] and using a discrete voxel approach [60]. The development of local feature manipulation in LCEs is reviewed comprehensively by White et al. [37].

Techniques for positioning constraining fibres and plates have a long history in manufacture, primarily for reinforcing composites. Two-dimensional orientation dominates, although ultimately, as in nature, three-dimensional structures are required to respond to forces from all directions and so this is a natural final goal. Embedding of rigid units into polymers has been demonstrated with high-aspect ratio silicon nanocolumns (HARNs) around which a hydrogel was formed. The result was HARNs embedded in the hydrogel in specific orientations, which altered with respect to each other in accordance with the degree of hydration of hydrogel [126], suggested for use in microfluidics. Magnetic field effects have been used to align micrometre rods and platelets with superparamagnetic coating in various polymers [183], which has enabled twisting and bending motions via the application of local constraint (Fig. 7). There is potential for combination of this method with slip casting to fill moulded structures [184], but evidently magnetic field manipulation is restricted to strongly paramagnetic materials.

A more general approach has been demonstrated to position reinforcement fibres within a polymer matrix using ultrasound; [185] this allows arbitrary orientation in two dimensions and some degree of

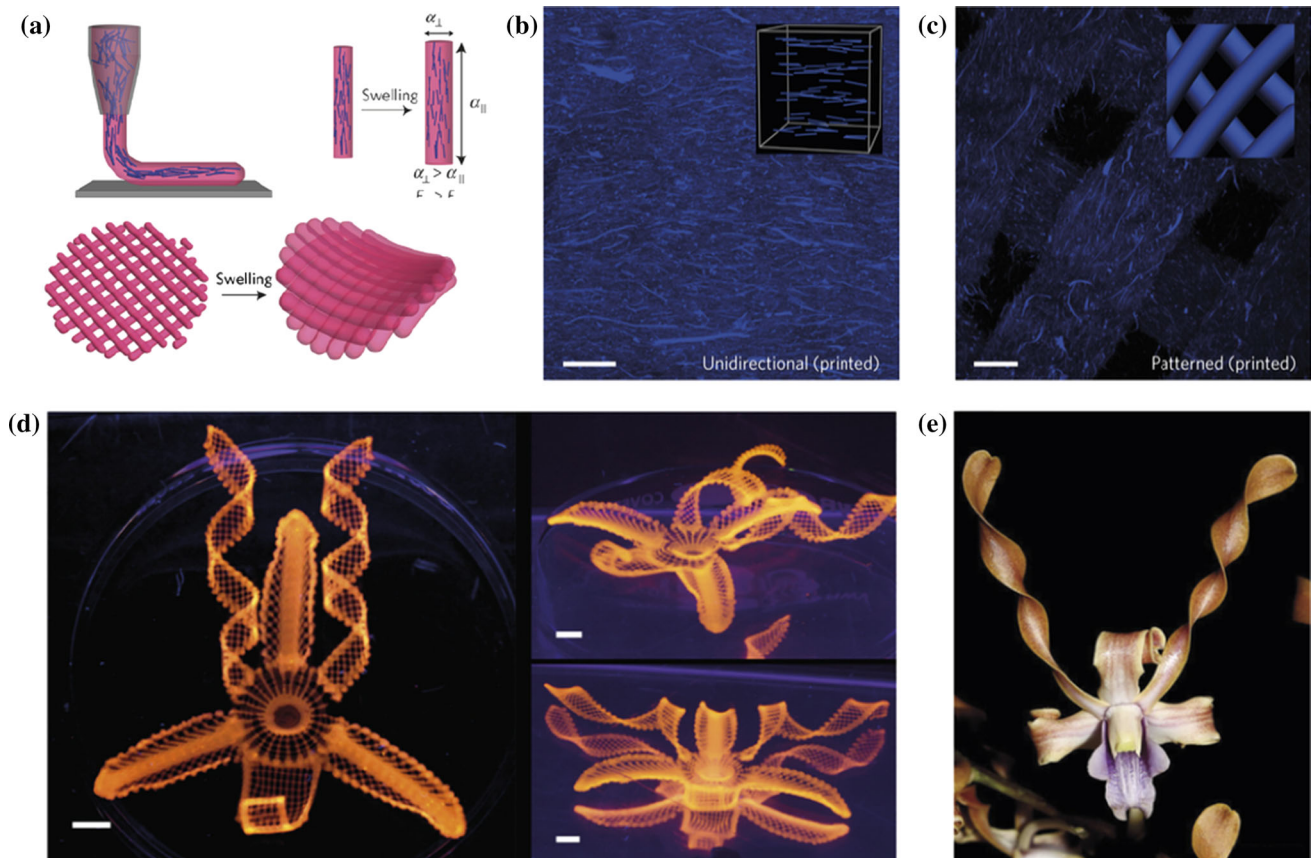


Figure 8 Directional fibre orientation via extrusion, by Lewis et al., used to replicate complex orchid curvature and shape. **a** alignment during printer extrusion and the mesostructure which translates this into programmed curvature. **b**, **c** The cellulose alignment achieved during printing (scale bar 200 μm). **d** Multiple

different shape-changes when immersed in water (scale bar 5 mm), in emulation of **e**, the dendrobium helix orchid. Adapted from Nature Materials with permission from Macmillan Publishers Ltd. [190] Copyright 2015.

positional control, and is suitable for any material as long as it differs in density to the matrix. Future challenges involve extending this to three dimensions and accessing orientations which cross between layers.

The alignment of fibres in the direction of extrusion shows great potential when combined with 3D printing technologies. This has hitherto been a subject of research for stiff materials; for example, carbon nanofibers added to ABS printing were shown to align with the direction of extrusion. The bar samples produced showed decreased swelling and greater tensile strength, although at the cost of increased brittleness [186]. More complex extruded honeycomb structures rendered in resin with aligned fibres delivered a superior Young's modulus for the lightweight samples, compared with other printing materials and natural balsa wood [187].

In softer materials, the addition of woven fibres has been successful in reinforcing hydrogels for strength [111] and directional confinement [188]. The alignment of constricting nanofibres within responsive electrospun polymer threads is a rapid way to generate hydrogels with ply angles analogous to those of classical composite design [189]. However, recent work by the Lewis group at Harvard's Wyss Institute (Fig. 8) has taken this work into another elegant dimension, deriving mathematical models that allow the construction of arbitrary-curved shapes through the precise control of cellulose fibre direction, given by the path of an extrusion-based 3D printer [190].

Extension of these orientating techniques to three dimensions would enable the creation of combined radial, longitudinal and helical fibres and structures; all key elements underlying the varied achievements of natural muscle, as exemplified by the hydrostatic skeleton [191].

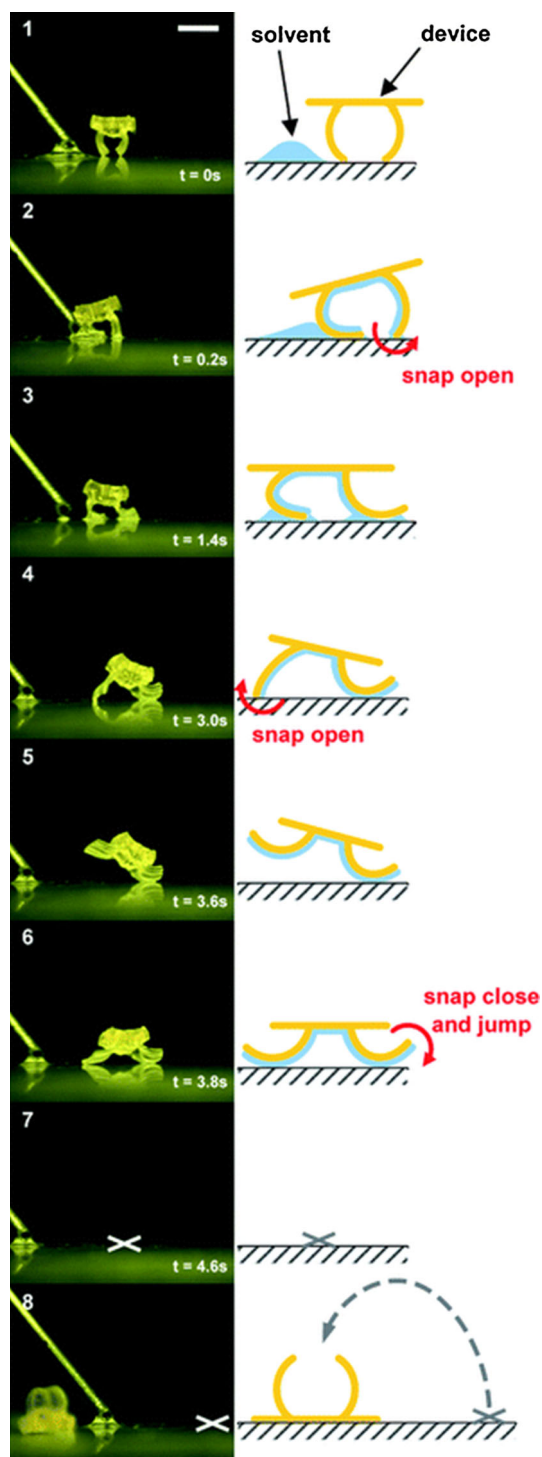


Figure 9 A biomimetic microgel, making use of microchannels and bistability, generates enough thrust to self-propel. The device is placed on a glass substrate (1). A solvent droplet fills the microfluidic network in the device by capillary action (2). Swelling results in bending of legs outwards (3–5). When bent, the device is ready to jump (6). Solvent in channels further evaporates, and snap-buckling takes place as the legs snap back to the original shape via de-swelling. This rapid motion produces enough thrust for the gel to jump out of the frame (7), landing outside the initial view field (8). Cross mark indicates the initial position of the device. Scale bar indicates 1 mm. Reproduced from Lee, Xia and Fang, with permission from the Royal Society of Chemistry. [204] Copyright 2010.

Creating bending and gradated response

Considering the system from a different perspective, one can abstract the concept of simply joining materials with differing responses to the same stimulus. The bilayer motif is found in nature (for example, the pine cone and Venus fly trap), in the classic bimetallic strip, and from the very beginning of work in hydrogel actuators [21]. This is a prototypical example in many papers demonstrating newly discovered actuating materials. Stoychev et al. have explored the shapes formed by bilayers with varying dimensions as a result of diffusion and surface interactions, using a combination of finite element modelling and experimental work [192].

Lithographically patterning a bilayer structure introduces an extra dimension to bilayer fabrication, as shown by Bassik et al. [193]. Only those areas exposed to polymerising UV remain attached to the bottom layer, thus creating a surface with some bilayer bending regions and some monolayer flat regions. This is used to create an all-hydrogel version of a Venus flytrap. In another example of two-dimensional patterning, Andres et al. localise inkjet deposition of carbon nanotube composites within a polymer, creating folding regions with reduced hygroscopic swelling (as hinge points) [194].

More complicated curvature from a two-material system was demonstrated by Wu in 2013 [121], where

hydrogels with thin, directed stripes of alternating chemical composition and coefficient of expansion were used to create complex deforming surfaces. The relatively small lateral modulation involved is directly reminiscent of plant motion, where, as in nature, small effects add up to create an overall larger movement.

A natural development from narrowly spaced alternating stripes is the transition to a continuously varying spatial response. This may be a gradient in composition; a natural example would be the combination of Type I and Type II muscles, whose different metabolic processes and response rates enable the many different behaviours required of skeletal muscle by changing the ratio of just two components [195]. Alternatively, it may be derived from structural variation or local amplification of a global stimulus.

The first case, of varying composition, has been realised in many different synthetic systems (see for example, Yu et al. with SMPs [196] and Maeda et al. with polymer gels [144]). A simple case is the variation of monomer concentration: gradients in monomer concentration throughout the injection forming of NIPAM sheets may be used to program the Gaussian curvature in a circular sample, allowing the spontaneous formation of domes and hyperbolic frills when heated [197]. Another approach is to introduce a second molecular species; for example, limited diffusion of a second polyacrylamide monomer into a pre-existing NIPAM gel is used to construct a bilayer strip and a flexible ‘hand’ gripping unit [21]. The gradient may also be created via post-treatment. For example, Zhao et al. expose a porous polymer network to a deprotonating acetone diffusion gradient, which causes variation in the degree of electrostatic complexation across the hydrogel and therefore its swelling response [119].

Structural modifications may result from altering the density of cross-links [22, 123] and the size of pores in hydrogels [198]. A more complex approach post-cured an SMP on a spatially varying thermal gradient, grading the glass temperature spatially and thus modulating the temperature at which different regions of the material regain their original shape [199]. Inert surface features such as a layer of micropillars can also direct the direction of deformation [46].

Finally, local amplification may derive from simple changes in colouration [200], or increased energy transmission induced by particles with a tailored surface plasmon resonance [155].

Form: a final boost to shape-change

Multifunctional materials exist to overcome the limitations of form. The sea cucumber not only needs a hard, defensive skin to resist ocean currents and predators, but also a soft, compliant dermis to take up shelter through narrow gaps in corals and to perform defensive evisceration [201]. Evidently, it can only have one skin, so the solution is to vary its stiffness, shifting between a tensile modulus of 5 and 50 MPa by modulating the interactions of collagen fibrils within the material [201]. This has been successfully emulated by Shanmuganathan et al. by the hydration-moderated interactions of cellulose nanowhiskers in low-density polymers [202].

Here, therefore, we see an example of material overcoming limitations of form. But the opposite situation can also be true: form may overcome the limitations of materials. Structural features, such as bistable shells [94], flexing keels [203] or collapsible chambers [92], expand the properties of materials through the structures they are formed into.

An example is an excellent final illustration of our journey through the materials, triggers and forms that can enable shape-change in soft materials. As discussed earlier, the variety of hydrogels available, combined with the many techniques for introducing anisotropy into their bulk, makes them an attractive material for volume-change-based actuation. However, the material experiences slow deployment times, as expansion is a diffusion-limited process [107], and the force exerted is typically small.

A solution to a similar problem is seen in the Venus flytrap, where the relatively weak forces exerted by water swelling release built-in strain, triggering a switch between two local minimal energy conformations [94]. Lee et al. emulated this with a combination of vasculature and pre-stress in the material to create the ‘jumping hydrogel’ (Fig. 9) [204]. Mesoscale channels created lithographically within a small hydrogel sample localise solvent exposure and therefore nanoscale swelling. The smaller scale also reduces diffusion length and therefore actuation time. Expansion and extension in a targeted small region were sufficient to flip the macroscale object into a second stable position, attain a maximum angular velocity an order of magnitude larger than the biological system, and release sufficient energy to propel it into the air. As noted by the authors, this design overcomes two known issues with hydrogels,

namely their mechanical weakness and slow actuation, through incorporation in a wider system.

Conclusion

A primary aim of this review was to examine the functionality and activation mechanisms of synthetic shape-changing materials used by the scientific community and benchmark our current knowledge of self-shaping materials against the strategies found in nature. As one might imagine, the conclusion is unavoidable; there will be no single material and manufacturing method which achieves the self-shaping the engineering and scientific community desires. Instead, we need to combine techniques to overcome shortcomings.

Key elements that have emerged in this review are the potential of nanoscopic features such as contracting fibres (as seen in muscle) and restrictive plates (as seen in plant tissues) to instigate and direct motion. These nanoelements must be united in a structured network, through embedding in a matrix or otherwise, potentially also including secondary mesoscale features. With current technology and materials, creating nanostructured materials in complex shapes requires either multiple steps (e.g. alignment followed by assembly), or dual development of materials and manufacturing (for example, alignment of fibre constructs during additive manufacture) [138, 140, 143].

From the top-down, we should look to create structures that minimise the force required to self-shape, and where possible target and combine stimuli to maximise the magnitude of the trigger delivered. The complementary use of different stimuli, such as the application of magnetic fields to reduce the temperature required for SMP relaxation [114], is a promising area, as is the potential of electrical or optical stimuli for remote, directional and modulated control.

Two themes are discernible from these examples: the potential for synergy between materials and form, and the need for features crossing multiple length scales—which require collaboration between manufacture and materials development. We therefore suggest simultaneous development of techniques for structuring materials, and the materials they will be used upon, as a fruitful direction. Diversification through the use of multiple techniques to create structures across complementary length scales, and responding to multiple stimuli, will combinatorially expand what is possible in this field.

Development of novel self-shaping materials can be expected to unlock applications and designs not yet considered, with corresponding changes in quality of life, material sustainability and environmental benefits. We consider that hierarchical material features, from nano- to macroscale, developed side-by-side with minimal-force structural designs, have the highest chance of blending nature's responsive design space with the constructed world.

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Compliance with ethical standards

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